# Preparation And Characterization of Rice Husk Silica Compacts
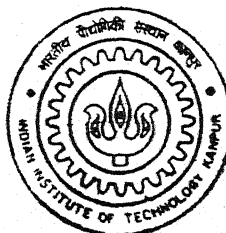
by

## Sagar Kashikar

DEPARTMENT OF METERIALS AND METALLURGICAL ENGINEERING
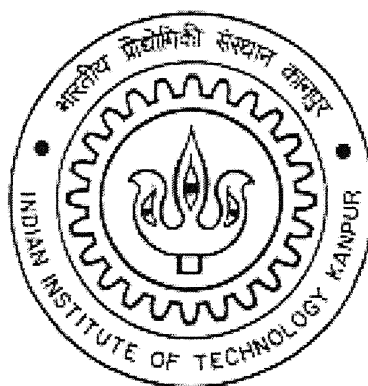INDIAN INSTITUTE OF TECHNOLOGY KANPUR
June, 2000

# Preparation And Characterization of Rice Husk Silica Compacts

*A thesis Submitted*
*in Partial Fulfilment of the Requirements*
*for the Degree of*
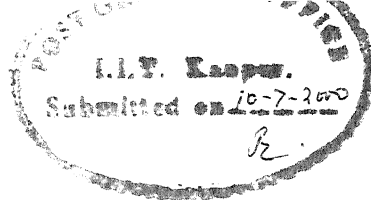
## Master of Technology

by

## Sagar Kashikar



*to the*

**DEPARTMENT OF METERIALS AND METALLURGICAL ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY KANPUR**

**JUNE, 2000**

# CERTIFICATE

It is certified that the work contained in the thesis entitled **"PREPARATION AND CHARACTERIZATION OF RICE HUSK SILICA COMPACTS "** by Sagar Kashikar , bas been carried out under my supervision and this work has not been submitted elsewhere for a degree.

Dr. K.N.Rai,

Professor,

Department of Materials and

Metallurgical Engineering

Indian Institute of Technology,

Kanpur, 208016.

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Dedicated
to my
Beloved Parents and Sister.

# Acknowledgment

I express my deep sense of gratitude to my advisor Dr K.N. Rai for giving me his guidance, constant support and encouragement.

I shall be failing to my duty, if I do not put on record that I am touched by a rare combination of excellence guide and human being in my advisor. Working with him was a learning experience in my ways that one. I shall consider myself fortunate if I can embibe some of his virtues in my life.

It is great pleasure for me to acknowledge the members of my group Anshuman, Amit, Rajesh and Mini who through their warm presence and words of encouragement always enlivened up the work atmosphere.

I pay my deepest sense of gratitude to all my teachers. I am also very thankful to Mr. Umashankar and Mr. I. Sharma whose sincere caring towards my project kept me in spirit.

I owe my caring friends and classmates Nacham, Rohit, Saumya and Somnath Das for providing encouragement and sharing the beautiful days here, it was they, who kept my spirits high.

It is difficult for me to find words to express my thankfulness to my *H-top* friends Advait, Lalit, Manoj, Ayush, Santosh, Roshan, Rajesh and Rakesh for the thoroughly enjoyable and memorable stay at IIT Kanpur.

Finally, I am proud of my parents and sister, whose love and blessings have enabled me to come this far.

# Abstract

Rice is one of the major crops grown throughout the world. After the separation of rice from the paddy , one-third of mass remains as a waste material. Many workers have tried to use this agricultural waste to produce useful materials such as silica, silicon carbide and activated carbon.

In the present work, an attempt has been made to focus all the work done in this area over the last ten year and study the formation of silicon carbide and silica in greater detail. The rice husk ash shows amorphous structure below sintering temperature of 800°C and cristobalite structure above it. The study has focused on specific surface area, porosity and dye adsorption property of pallets produced by mixing rice husk ash and sodium silicate (binder). These properties were found to decrease with sintering temperature of pallets. The pallet with low compaction pressure shows increase in density with sintering temperature. However high compaction pressure pallets show a decrease in density after 900°-1000°C. The pallets compressed at 2 Ton show increase in strength with sintering temperature. The pallets pressed at 4 – 6 Tons however shows a decrease in strength after 1000°C. The pallet containing medium binder showed maximum crushing strength at sinter temperature at 1000 °C.

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# CHAPTER 1

# INTRODUCTION

India produces more than 60 million tons of paddy annually. About 1/3 rd of the paddy is the husk, a waste material of the rice mills generally dumped or burned at the mill sites. The cumulative deposit of the enormous quantities of the husk is a matter of much concern because of the disposal problem and related pollution hazard.

This has led to spurt of investigations throughout the world to search for better products based on rice husk. The foregoing sections are therefore devoted to shed light on various aspects of work going on for synthesizing more and more new products. The important investigations are therefore presented below.

## 1.1 Thermal degradation of rice husk

Thermal Gravimetric Analysis (TGA) of rice husk has been carried out by Teng et al. [1] from room temperature to 1173 K at heating rates of 10, 30, 60, and 100 K/min. From the TGA, they noticed four different categories of lumps corresponding to the (1) evolution of moisture, (2) pyrolysis of hemicellulose , (3) cellulose and (4) lignin. The decomposition of each lump was characterized by a first order reaction with respect to the amount of volatiles present, having an activation energy of 48, 154, 200 and 33 KJ/mol respectively. Differential Thermal Analysis (DTA) of rice husk showed three important endothermic peaks at 370, 420 and 570 $^0$C, indicating that silica is present in three locations with different bonding energy [2]. Pyrolysis of rice husk hydrolytic lignin at 100-400$^0$ C and a heating rate of 2 deg/min was investigated by Saprykin et al. [3]. By observing the emission velocities of $CH_4$, CO and $CO_2$ with temperature, they determined the temperature range of the formation of carbon oxides and methane. The temperature range at carbon which oxides and methane are produced showed a maximum of 320-440$^0$ C and 380-450$^0$ C respectively. Thermal degradation of rice husk and hydrolytic lignin (from husk) was performed in air and

nitrogen. The main component was CO, $CO_2$ and low molecular weight hydrocarbons [4]. The higher the cellulose content of the rice husk, the higher the thermal degradation rate and initial degradation temperature [85]. Also, higher ash content in the rice husk resulted in higher residual weight at $600^0C$. Effect of pulverization on husk densities on morphologies has been attempted. It was found that morphology of the milled rice husk changed drastically. The density of milled rice husk was higher and increased with decreasing miller husk sizes [5].

## 1.2 Rice Husk Silica Production and Properties

Silica is an important ingredient in the production of glasses, cements and other refractories such as porcelain [15]. Normally it is obtained by pulverizing graded quartzite rocks. The powder production from hard quartzite rocks is a very high energy intensive process. Unlike this, silica from rice husk can be produced by simply burning in appropriate conditions. The energy is supplied from the carbonaceous part of the husk itself. Also, the silica produced in this manner is highly reactive, requiring minimum grinding. Therefore, attempt by many workers has been made to produce silica from rice husk. Hayashi et al. [6] have produced silica having large surface area and high porosity by burning rich husk. During the process about 20% mass of rice husk remains as ash, and it contains about 95 weight % of silica. High purity silica having purity of 99.99% was produced from the husk using $HNO_3$ and $H_2O_2$ in a definite proportion (rice husk/$H_2O_2$ = 1:50 by weight, $H_2O_2$/$HNO_3$ = 10:1 by volume) under optimum conditions (temperature = $150^0$ C, time = 3 hours) [7]. Cook et al. have produced biogenetic silica by feeding rice husk in an inclined rotary furnace at $450^0$ C, which was rotated at 1 rpm for 30 minutes [8]. Biogenetic silica of very high permeability was also produced [9]. It was found by Chakraverty et al. that leaching of rice husk with HCl at 75 $^0$C for one hour prior to combustion produces amorphous silica of complete white color [10]. Silica having purity of 92% and the average diameter of 0.04 to 0.05 micron was produced by Hwang et al. [11]. Their production of silica involved four stage i.e. feeding, combustion, spraying and drying. Studies of

of silica involved four stage i.e. feeding, combustion, spraying and drying. Studies of surface morphology (SEM), chemical reactivity and surface area measurement reveal the formation of amorphous silica during the ashing. The reactivity was found to be maximum at ashing temperature range of 400-600 $^0$C and holding time 6-12 hours. However, it was found to decrease with ashing temperature and hold time [12]. After comparing the X-ray photoelectron spectroscopy peak width of natural silica with those of rice husk ash, the authors [13] have attributed the differences in width due to variation in immediate chemical environment of silica and oxygen in the husk ash.

Rice husk ash produced in this manner can be used as a substitute for the production of porcelain [14]. It can also be used in the production of high silica zeolite of pentosil family [15]. Rice husk formed at 700 $^0$C is amorphous and can be used in the production of cristobalite [16]. Because of its high porosity and large surface area, it can be used to synthesize siliceous raw material such as clay mineral. Smecite was prepared from rice husk ash using Si, Mg, and Li [8]. Biogenetic silica can be used in industrial wastewater treatment [9]. Fukazawa [17] has prepared friction material having balanced energy absorption coefficient and other friction properties by compaction and press sintering (temperature = 750 –850 C, pressure = 1-10 MPa) of a mixture containing Sn (2-8 weight %), $SiO_2$ (2-10 wt %), graphite (18-33 wt %), rice husk (2-8 wt %) and rest electrolytic Cu powder.

# 1.3 Production of Silicon Carbide Ceramics.

Silicon Carbide ceramic can be used in variety of applications, such as furnace heating elements, abrasive applications, high temperature semiconductor and as construction material[19]. SiC based ceramic carriers for immobilization of micro-organism can be used in petrochemical wastewater treatment [24]. Ceramic bricks having very high compressive strength and good water absorption (20 %) has been found to be useful in load bearing walls [24].

Rice husk contains both the ingredients (Silicon and Carbon) necessary for the production of Silicon Carbide. Steam expansion treatment of husk therefore, has been used to produce Silicon Carbide. The process involved steam expansion (10 – 30 $Kg/cm^2$) treatment of husk at 150-230 $^0C$ for 30 minutes followed by hot pressing at 150 Kg/cm2 after pyrolysis at 500-700$^0$ C. The above process is found to be effective in (i) solubilization and depolymerization. (ii) concentration of silica in the treated husk. (iii) decrease in $C/SiO_2$ ratio of the pyrolyzed residue and (iv) minimization of carbon content in the final Silicon Carbide materials [18]. Yoshikawe et al. [19] have produced porous silicon carbide ceramics by coating rice husk powder (40 μm) with a solution of carbonizable thermosetting resin followed by moulding, firing (temperature = 1500-1800 $^0C$, non-oxidizing atmosphere) and refiring in air (to remove residual carbon). High-grade silicon carbide of 99.7% purity was prepared by reacting the product obtained after supplying rice husk ash and a binder containing coal tar (or high siliceous clay) in a gasification furnace at 1700-2100 $^0C$ with reaction time of 3 hours [20]. Vlasov et al. [21] has attempted to synthesize fine grain powder (1-2 μm) and fibers (apex ratio = 5-20) of Silicon Carbide by treading rice husk and it's hydrolysis product lignin at 500-800$^0$ C in nitrogen and air. Cheng et al. [84] synthesized 50-70% SiC from rice husk by crushing, acid treatment and $FeC_{12}.6H_2O$ impregnation. Then it is filtered, dried, decomposed at high temperature, synthesized and HF treated. He discussed the effect of $FeCl_2.6H_2O$ impregnating time, mineralizer, reaction temperature and CO atmosphere on synthesis of Silicon Carbide. Rambo et al. [86] exposed rice husk to microwave energy (2.45 GHz) in different atmosphere to promote the reaction between C and $SiO_2$. $SiO_2$ reacted with C to form B-SiC whiskers. The amorphous $SiO_2$ was transformed to a ∝-cristobalite in this process.

## 1.4 Activated and White Carbon Black

Yu et al. [26] have developed a new technique for the production of high a quality white carbon black by precipitating hydrated Silica ($nSiO_2.xH_2O$) using reaction between carbonized rice husk and $Na_2CO_3$. The importance of this technique is high yield (90 %) of white carbon black and reusability of $Na_2CO_3$ solution. Wei et

al. [27] have also attempted to produce white carbon black (porous silica by igniting purified rice husk to whitening combustion in a rotary furnace. A process for the production of both white and activated carbon was developed by Liu et al. [28]. They produced white carbon by heating a mixture of carbonized rice husk (temperature=600-650$^0$ C) and $Na_2CO_3$ solution (8-11 baume) in ratio of 1:37 for 3-3.5 hours at 120-130$^0$C followed by neutralization with 25% HCl. This white carbon after acid washing and purifying was heated at 650$^0$ C for 15-18 minutes to produce activated carbon. Granular Activated Carbon (GAC) was produced by Usmani et al. [29] from high and low ash rice husk using $ZnCl_2$. Here $ZnCl_2$ acts as an activating and as well as binding agent.

The physical (bulk density and hardness) and chemical (pH and mineral content) characteristics of granular activated carbon made from rice straw, pecan shells hulls of soybean and rice were found to be useful in raw sugar decolorization [30]. Youseef et al. [31] have studied the surface properties of $ZnCl_2$ on steam activated carbonized (temperature = 863 $^0$C) rice husks. Specific surface area of the carbon prepared and the changes caused by activation were determined by nitrogen adsorption at 77 K or carbon dioxide adsorption at 298 K and methylene blue from aqueous solution at 303 K.

# 1.5 Molds, Clays and Cement

Molds of rice husk compounded with different substances shows good properties such as compressive strength, heat and warping resistance. Molds of a mixture of cement and dried rice husk (volume ratio = 1: 3) having water-cement ratio of 0.4 to 0.6 were manufactured by Iwayama et al. [32]. They poured the mixture into cylindrical molds and cured it under pressure at a compressive ration of 1.1 to 1.4. Tough moldings from a mixture of propane polymer (100 parts), maleic anhydride I-grafted propene polymer (1-25 parts), glass fibers (5-100 parts) and rice husk (1-75 parts) were manufactured by Shiraishi et al. [33]. Tough moldings were also manufactured by these workers by palletizing a mixture of MS 684100, I-grafted

polypropene (7 parts) crushed rice husk (1- parts) and glass fibres (30 parts) at 180 C followed by injection molding at 220 C. Molding of a mixture of glutenes (100 parts) with nontoxic polyalcohols hydrophilic plasticizers (15-40 parts) and edible fillers ( less than 40 parts) was found to give golf tees [34]. Watanable et al. [35] have attempted to obtain the compositions from monolithic (magnesium oxide, mullite or chamote) refractories, by mixing crushed rice husk (1mm) with (1-100) weight parts of refractory material. Aqueous solution of 10% rice husk was used in the manufacture of polymer-bonded clay [36]. Painuli et al. [37] have studied the use of natural substances (coarse and fine rice husk, sawdust) and synthetic organics (polyvinylalcohols, polyacrylamides and polyvinylacetates) to improve the aggregate stability of sodic sandy loam solids, Rice husk was used as a source of siliceous material for the manufacture of carbon containing silicate molded bodies having density of 0.1 $g/cm^3$ , binding strength 6.2 $Kg/cm^3$ and drying shrinkage of 0.27 % [38].

Molds prepared from rice husk and propene polymer was found [33] to show good heat and warping resistance. Many of product showed 0.5% warping after 48 hours at 23 $^0C$ at 50 % relative humidity, with a flexural modulus of 38900 $kg/cm^2$ with heat distortion temperature of 139 $^0C$. Dry powdered plant fibers of golf tees can be used as a filler [34]. The use of rice husk in place of conventional fibrous additives improved the flowability, heat insulation and workability of the refractory composite [35]. Polymer bonded clay manufactured from rice husk showed good gloss, water and abrasion resistance. This can be used for surface treatment, waterproofing and mothproofing of articles [36]. The stability of sodic sandy loam solids was found to increase by incorporation of rice husk and organics [37]. Concrete surface cleaning compositions were investigated by Ookawachi et al. [39] using materials (sawdust, powdered cellulose, powdered rice husk) containing powdered detergents and colorants. Good quality surface decorative and surface finishing boards were prepared by binding rice husk with formaldehyde-urea resin binder or with caustic magnesite powder and with $MgCl_2$ as binder[40].

Barkakati et al.[47] have used the calorific value and reactive silica of rich husk for making portland cement. The use of rice husk decreased the production cost, since it decreased both the fuel and silica consumption. It was observed by sugita et al. [48] that the addition of rice husk to cement not only increased toe concrete strength but also it's resistance to 2% HCl solution attack, Cl- penetration and carbonation. High calorific value of carbonized rice husk decreased the energy consumption of black meal process of cement manufacture by 50% [49]. Stav et al. [87] show the use of rice husk ash as a cementitious binder which also includes $\beta$-$CaSO_4$ hemihydrate. Bui et al. [88] showed that the application of the RHA in conjuction with naphthalene based superplasticizer in the gap-graded concrete with very fine sand made it possible to produce high consistency and cohesive mixture with a relatively low sand content. 28 days compressive strength values of 70-90 MPa were obtained for mixtures with slumps of 140-225 mm and water to binder ratios of 0.40-0.3 . Shuichi et al. [89] prepared concrete specimens with different RHA blending ratios at different water-cement ratios then cured in water, 2%HCl solution and an accelerated carbonating chamber, respectively. The result shows that after the addition of RHA to the cement, the strength of the concrete was enhanced greatly. Also losses of mass and strength of the concrete cured in the HCL solution and the carbonization rate of concrete were decreased. It was also observed that the resistance of concrete to the penetration of water, air and chloride ion can be much improved by using RHA. Stroeven et al. [90] shows that addition of RHA to portland cement increases strength with water reducing agent at low water-cement ratio. Qijun et al. [91] confirmed that at $40^0$ C and in the presence of water, the amorphous $SiO_2$ contained in RHA reacts with Ca (OH) 2 to form one kind of C-S-H gel. ( $Cal_5$ $SiO_{3.5}$. $xH_2O$) . The improvement of concrete properties upon addition of RHA may be attributed to the formation of more C-S-H gel and less portlandite in concrete due to reaction occurring between RHA and Ca2+, OH- ions, or Ca $(OH)_2$ in hydrating cement.

# 1.6 Fertilizer Blends

Various types of fertilizer for agricultural use were prepared from rice husk using different techniques. Coated fertilized having controlled release have been produced by Yokota et al. [41]. They found that the presence of rice husk slowed down the release of fertilizers. Rice husk was formed into packaging members of pellets, which were found to be biodegradable and can be used as fertilizer [42]. Yamada et al. [43] have produced slow release type of fertilized by heating philippine dolomitic limestone, rice husk and potassium carbonate at 700-900 C in air. For fertilizer to be effective, the molar ratio of ( $CaO + MgO + K_2O$)/$SiO_2$ was found to be in the range of 2.0-2.5.

# 1.7 Fuels and Process Ingredient

Rice husk is widely used as a fuel and temperature control agent in various processes. Cast iron feed was produced by the melting iron base scrap in an electric submerged arc furnace using rice husk. The efficiency was upgraded from 60-65% in a small furnace to 80-90% in a big furnace [44]. Suzuki et al.[45] have used burnt rice husk as a source of carbon to prevent the decrease in temperature of molten pig iron in steel making. Pelletization followed by reduction (CO atmosphere, temperature = 1100-1500 $^0$C) and purification (sulfur removal) of a mixture, which contains powdered iron ore, rice husk and binder (bentonite) was done. This was found suitable for the production of sponge iron [46]. Use of boiler fired rice husk B. Singh et al. [50] resulted in the improvement of clinker quality and reduction of fuel consumption. Rice husk fired at $450^0$ C with portland cement forms pozzolanic cement, which combination with water and lime at room temperature forms compounds with cementing properties [51]. Composite solid fuels were prepared by mixing rice husk with combustion aids (dolomite, lime, slag, $NaNO_3$, $Fe_2O_3$) [52]. Klatt et al. [53] have used rice husk as thermal barrier by packaging it in the hollow areas of building at pressure 200-250 $Kg/m^3$.

# 1.8 Production of Lignin and Cellulose

Mainly the process of hydrolysis has been carried out to produce lignin, cellulose and other related products. Kaglunova et al.[54] have carried out demethoxylated lignin catalyzed hydrogenolysis of protolignin, hydrolytic lignin and dioxane lignin from rice husk. They found that the demethoxylated lignin catalyst acted similarly to other catalyst used for above purpose. Moya et al. [55] have attained the maximum bezylation functionalization and yield of lignocellulosic wastes (pineapple, peel, rice husk, sawdust) by treatment of NaOH slurries at 90-100 $^0$ C for 8 hours. This was further dried, milled to particle size of 0.25 mm. The cellulosic material obtained after extraction was bleached with 2.5% NaClO solution for 4 hours at ambient temperature. The degree of Benzylation was determined by infrared spectra of the cellulosic material. Condition for cellulose production and other hydrolysis product from rice husk has been investigated by Wang et al. [56]. The optimum condition for cellulose production were reported as follows:

(a)     ratio of straw to wheat barn=7:3,

(b)     water content of the solid state medium of straw powder and wheat barn=250 %,

(c)     pH = 6.0 to 6.5,

(d)     temperature=30 $^0$ C and

(e)     incubation time=3 days.

The optimum conditions for the hydrolysis of rice husk were found to be:

(a)     proportion of barn of rice husk= 1:3,

(b)     temperature 40 $^0$ C,

(c)     pH = 4.4 and

(d)     incubation time = 3 days.

Extraction of rice husk with hot water was found to give polysaccharide, which on hydrolysis resulted in the formation of D-mannose, D-glucose, L-rhamnose and D-galactose. On carrying out methylation followed by hydrolysis, preparation of alditol acetates and gas-liquid chromatography, it was found that the D-mannose, D-glucose, L-rhamnose and D-galactose units are 1, 4 linked with D-mannose unit at

terminal [57].Hydrolysis of rice husk with oligosaccharides to manmos
hydralyzate was found to contain higher amount of monosaccharides. The
acid catalyzed hydrolysis of hemicellulose-polysaccharide complexes obta
husk of sunflower; rice and cotton have been studied by statalov et al. [59].

Hydrolysis product obtained from rice husk can be used for many ap]
Bezyalted lignocellulosic materials can be used in manufacture of plastic [
husk hydrolyzate obtained in presence of obligaccharides extraction water ca
raw materal for manufacture of fodder yeast [58]. The cellulose material
from rice husk can be used to remove Ni and Cu ions from solution [60].

## 1.9 Production of Organic Compounds

More organic compounds were synthesized using rice husk. A m
manufacture of furfural by direct hydrolysis of wood particles or rice or sɪ
husks in steam was developed by Sobolev et al. [61]. Oxalic acid in high y
purity was manufactured by Mane et al. [62] by oxidizing agricultural was
concentrated $H_2SO_4$ and $V_2O_5$.Pyrolytic oils containing naphthalene, fluor
phenanthrene were obtained during the pyrolysis of wood wastes, municip
waste and rice husk in a glass-purged static bath reactor and fluidized bed reacɪ
oil separated into different classes [63]. Various amounts of phenols,
compounds and acids were also obtained during pyrolysis of rice husk at 3
$^0$C[64].

## 1.10 Production of Inorganic Compounds

Rice husk can be used as a raw material for production of many inc
compounds. Suda et al. [65] have manufactured silicic acid by immersing cɦ
heated solution of 2% NaClO and 4% NaOH followed by the addition of conc. Ħ
Calcium hydrogen phosphate was produced as a byproduct (yield=10%) c
separation of vegetable casein from chaff [66]. Both the alpha and beta phase dɩ
of fibers of $Si_3N_4$ was prepared from acid treated rice husk by Patel et al.[67].The

of fiber is due to the absence of fiber substrate in rice husk which were degraded during acid digestion. $Si_3N_4$ fiber were obtained by continuously moving rice husk inside a heating zone at temperature 1300 $^0C$ in nitrogen atmosphere [68].Chen et al.[69] have used rice husk's carbon and silica for the production of $SiCl_4$.High purity silicon was produced from ash of rice husk by leaching, ashing at 620 $^0C$ and thermal reduction in presence of Mg[70, 71].Nandi et al.[72] have used magnesium silicide from rice husk for the production of silanes. They also optimized acid concentration, temperature and particle size of magnesium silicide from rice husk for the production of silanes. Rice husk ash was used as a source of silica for the production of choline chloride powder[73] and high crystallinity zeolites[74]. Popoola et al.[75] have manufactured a series of dyes based on sulphur chromophores using baking process involved in rice husk. Wallastonite was manufactured from the rice husk ash by Hevia et al.[76].Here rice husk was used because of two reasons; firstly it provides silica and secondly it is more economical and easily available.

## 1.11 Production of silicon from rice hull

Amick [93] shows the way for producing solar grade silicon for solar cell from the rice hull. He suggested that although the metallic impurity concentration in raw hull is high, it can be reduced to less then 1ppm by extraction in hot aqueous HCL followed by pyrolysis in a ambient containing anhydrous HCL .The carbon to silicon ratio in a pyrolyzed hull can be adjusted, either by partial combustion of carbon or by addition of suitable silica source. Thus the material offers promise for the low cost source of silicon suitable for preparation of solar cells. Again Hunt et al. [94] extruded pellets of coked rice hull, with sucrose as a binder, were shown to be very reactive row material for the production of silicon using techniques of submerged electrode and arc furnace technology. A short duration arc-furnace experiment using these pellets resulted in lowest energy consumption ever measured in this furnace. Acid leaching of rice hulls was demonstrated to produce much purer coked material. It can be

projected that an acid-leaching and coked product is of interest as a row material for the production of solar-grade silicon.

## 1.12 Gasification for Power Generation

Salvi[77] has attempted to study the rice husk gasification for power generation. He installed a down flow fluidized bed gasifier, equipped with a rotating grid at the bottom for continuous removal of ashes. The gasification was carried out at a temperature of 1000 $^0$ C .The process consumed 150-160 Kg. of rice husk per hour giving rise to fuel gas yield of 350 $m^3$ /hr with a heating value of 1000 Kcal/$m^3$. The gas obtained was purified by filtering through rice husk and was fed into an otto generator with controlled combustion to generate 80 Kwe. Chowdhary et al. [78] have developed a mathematical model to study kinetics and mechanism of reaction occurring during gasification of rice husk. The simulated temperature profiles and gas composition were compared with cylindrical updraft moving bed gasifier. Following were the gasification conditions: gasification rate rate of 3.5-12.5 at 10-30 Kg/$m^2$s and air flow rate of 0.07-0.11 m/s for generation of producer gas with heating value of 3712-4464 KJ/$m^3$. Model was found suitable for the representation of engineering processes. Nijaguna et al. [79] had build an atmospheric pressure fluidized bed combustor for the utilization of charcoal and agricultural wastes (coconut shell, bagasse, sawdust and rice husk) with air as fluidizing agent and sand as a support for fuel. A model of an open core down draft moving bed rice husk gasifier was developed by Manurung et al.[80] to predict its performance as a function of operating variables like heating rate, feed properties etc. The model was based on mass and energy balances, reaction kinetics, transport rate and fundamental thermodynamics relations. The electric power generated can be used as a stand alone system especially for rural areas [77]. The open core down draft moving bed rice husk gasifier model can be used to predict the effect of changing operating parameters and feed properties [76].

# CHAPTER 2

# PRODUCTION OF SILICON CARBIDE AND SILICA FROM RICE HUSK

This chapter mainly deals with procedure adopted for the production of silicon carbide(SiC) and silica($SiO_2$) from rice husk. Due to inherent difference in chemical composition of SiC and $SiO_2$, temperature processing also differs significantly. Those are therefore being presented in following section more elaborately.

## A. Production of Silicon carbide

## 2.1 Principle of Production

Rice husk char is prepared by heating the rice husk at 600° C. Then these samples are heated 1180° C, 1250 °C, 1280° C and 1380° C with charcoal under vacuum. Rice husk have an advantage by yielding amorphous silica and carbon, both of which have measurable higher free energies than quartz and graphite upon which the usual thermodynamic calculation are based. It is estimated that amorphous silica and carbon may shift the equilibrium towards silicon carbide by approximately 100° C lower than for quartz and graphite [95].

The SiC formed on the carbon surface. The reaction could proceed via the gas phase by dissociation of silica, and subsequent reaction with carbon. Hence, the SiC formation can be divided into four reaction steps as [95]:

$$SiO_2 \rightarrow SiO + 1/2\ O_2 \qquad (1)$$
$$1/2\ O_2 + C \rightarrow CO \qquad (2)$$
$$SiO + C \rightarrow Si + CO \qquad (3)$$
$$Si + C \rightarrow SiC \qquad (4)$$
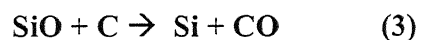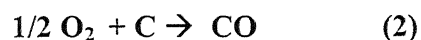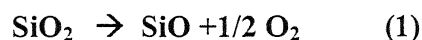
Considering the free energy of reaction, the first reaction is most difficult, however, more evidence is needed to decide the rate controlling step, since thermodynamic calculations are not sufficient to predict the reaction path and velocity without kinetic implementation.

An attempt to find out the slower step was carried out by observing the effect of particle size of Silica on the rate of SiC formation. As summarized in Table I [94], there was a significant increase in the SiC formation with decreasing silica particle size, while other factor remains the same. Reaction (1) is the only reaction dependent on surface area of silica, which leads support to the postulate that SiO formation is rate-controlling step.

Table I: Effect of Particle Size of Silica on the formation of silicon carbide [94].

| Sample | Temperature ($^0$C) | Atmosphere | Time (min) | SiC Yield |
|---|---|---|---|---|
| Charcoal (70 μm) Quartz (40 μm) | 1470 $^0$C | Ar | 30 | 29.0 % |
| Charcoal (70 μm) Sand (800 μm) | 1470 $^0$C | Ar | 30 | 1.8 % |

## 2.2 Procedure for Production of Silicon Carbide

Production of SiC from rice husk has been carried out in two steps. Firstly the production of rice husk char followed by reduction of charred to SiC in the second step these are being produced below in more detail.

## 2.2.1 Preparation of Charred Samples

The rice husk was obtained from rice mill of Barasirohi village (Kanpur City)cleaned from foreign materials such as dry leaves and other additives. About 50

gm of rice husk taken in crucible for char production. The husk in crucible was heated slowly to 600 $^0$C in air for about one hour. For each time about four charred samples were produced for further work.

## 2.2.2 Silicon Carbide Production From Rice Husk Char

These charred samples were evenly mixed with coarse charcoal (size 5-10 mm). The charcoal is used to produce reducing condition. The charcoal mixed char was kept in a silica tube (one end closed) of 1-inch outer diameter and connected to vacuum pump for continues evacuations. The evacuated silica tube containing above mixture was heated to a temperature of 1180, 1250, 1280 and 1380 $^0$C. The holding time was 2 hours. The silica tube containing sample was remained in furnace and it was cooled to room temperature after switching of the power supply.

The powdery substance remained from the tube was then subjected to optical and scanning electron microscopy after the visual observation.

## B. PRODUCTION OF SILICA FROM RICE HUSK

Silica sintered compacts were produced in three stages. Firstly the production of white ash. Second step was mixing with sodium silicate binder and compaction.
In third step it was sintered at high temperature to produce silica sintered compact. They are presented here in more detail

## 2.3 White Ash Production

The production of white ash is comparatively more difficult due to constrained kinetic condition. The electric oven is used for heating purpose. Cleaned rice husk is spread uniformly on a wire mesh, which was kept on electric oven. The loading thickness was minimized to allow maximum oxidation during firing. In order to enhance oxidation kinetics further air was blown on the rice husk heap during firing.

Air blower is used for producing the draft of air. It is kept at 30-40 $^0$ to the wire mesh surface so that it can cover maximum surface. Another mesh is kept on the rice husk so that the ash should not fly out. The heating temperature is 800 $^0$C .The heating and blowing is continued for about 2-3 hours until the blackened rice husk ash was not turned into white.

## 2.4 Production of Compacts

The cylindrical compacts were made from rice husk for further studies. It was carried out by hydraulic press. The ash was crushed and mixed with 10% sodium silicate solution, which is act as a binder. The 10% sodium silicate solution was produced by dissolving 10ml sodium silicate in water, which was diluted to 100ml. The binder content is varied from low (8%), medium (16%) and high (24%) to investigate their effect on sintering. The pressure of compacting is also varied from 2, 4 and 6 tones for different samples. Thus for three variation of binder, three variation of pressure and four variation of temperature (i.e. 800, 900, 1000 and 1100 $^0$C), thirty-six sample are produced. Then they are dried on hot plate to remove moisture. The height, diameter and weight are calculated for each sample.

## 2.5 Sintering of Compacts

The sample consist of different amount of sodium silicate binder and pressed at different preset pressure was produced. The heating is carried out in tubular muffle furnace. The holding time for each sample is two hours. Air atmosphere is used for sintering. After sintering the samples are cooled in air. Again the height, diameter and weight are measured and density is calculated.

# CHAPTER 3
# EXPERIMENTAL TECHNIQUES

This chapter mainly deals with methods of characterizing the product of present investigation namely the silicon carbide and silica. Main methods used are scanning electron microscopy, X-ray diffraction, BET and dye adsorption. Details of these methods are presented below in the following section.

## 3.1 Scanning Electron Microscopy (SEM)

Scanning microscopy has been used primarily to examine the topology of surfaces. In this case the sample is in form of flakes. So we followed the procedure of analysis of powder sample.

### 3.1.1 Sample Preparation

The sample preparation is very crucial step in SEM examination. Firstly the 10mm diameter round step was taken. Then flaky sample is mounted over it. It was coated with Au-Pd just for making it conducting. This was carried out in sputtering unit for about 30 minutes. Then the sample was loaded in SEM. The voltage was 15KV and working distance is 37mm.

### 3.1.2 Image formation

In scanning electron microscopy (SEM), the electron optics acts before the specimen is reached to convert the beam into fine probe, which can be as small as $100^0$A in diameter at the specimen surface. As the probe is scanned over the specimen surface by deflection coils, an image may be formed by collecting scattered radiation signals (backscattered electron, emitted X-rays or optical photons) by suitable detector and displaying this signal in a raster synchronous with that probe. The incident electron beam causes the emission of secondary electron, auger electrons and

characteristics X-ray that can be analyzed to provide additional information about the area of the sample of which a SEM picture is obtained.

## 3.2 Surface Area Measurements Using Gas Adsorption

The most common method of measuring surface area is that developed by Brunauer, Emmett and Teller (BET) using gas adsorption at liquification temperature (Boiling Point). They derived following equation for adsorption isotherm relating the volume V of adsorbed gas at pressure P of the molecule in the gas phase

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} * \frac{P}{P_0}$$

Where

$P_0$ = saturation pressure of adsorbate gas at boiling point,

V = volume of gas adsorbed at pressure P,

$V_m$ = Volume of gas adsorbed in monolayer,

C = a constant,

A plot $\dfrac{P}{V(P_0 - P)}$ verses $P/P_0$ gives a straight line with slope $S = \dfrac{C-1}{CVm}$ and intercept

$i = \dfrac{1}{CVm}$ . The inverse of the sum of these two gives the monolayer volume ($V_m$) of gas adsorbed on the surface. On substituting the value of $V_m$ in intercept, one can obtain the value of C. From $V_m$ one can calculate the number of molecule 'n' absorbed i.e.

$$n = \frac{V_m N_o}{22414}$$

Here 22414 corresponds to volume in cm$^3$ for one gram mole of the adsorbate gas, Surface area per gram 'S' can be calculated by multiplying n with area ($A_m$) occupied by one molecule of adsorbent, divided by the mass of the material M under investigation

$$S = \frac{Vm.No.Am}{22414.M}$$

$N_0$ = Avogadro number

$A_m$ = Area occupied by one molecule of absorbent

For Nitrogen at it's boiling point, the value of Am used is 16.2 A$^{02}$ or 16.2 X 10$^{-20}$ m$^2$.

## 3.3 Pore volume determination

Total pore volume is determined by measuring the total adsorbate volume at a relative pressure ratio (P/P$_0$) as possible close to unity to include the large radius pores in the measurements. If Wa gm of nitrogen is adsorbed at P/P$_0$ = 0.99, then the corresponding volume of pores Vp is given by

$$V_p = \frac{W_a}{\rho_l}$$

Where $\rho_l$ is the liquid nitrogen density.

In the present investigations COULTERtm SA3100tm series was used for surface area, pore volume and pore size analysis.

## 3.4 Compression Strength Test

Compression strength test is carried out on INSTRON 1195.The load was applied perpendicular to flat-faced cylindrical sample of diameter 13.25mm and height

about 11-13 mm till it breaks. The load divided by original cross sectional area gave the compressive strength of the samples.

# 3.5 X-ray diffraction

X-ray diffraction in the present investigation has been used to resolve two important issues. First it has been utilized to observed the crystal structure of the rice husk silica in as prepared state and as a function of processing parameters of compacts. Secondary the particle size of the silica as a function of sintering temperature was also investigated. The experimental details are presented in following sections.

## 3.5.1 XRD For Structure

The powder samples are used for X-ray diffraction analysis. These power samples were produced by grinding sintered compacts in grinder. Then it was mounted in 1cm×1cm square stage. It was loaded in X-ray diffractometer,

X-ray diffraction pattern of samples with different composition and sintering temperature were recorded by ISO-DEBYFELX at following working parameters.

| X-Ray    Source | CuKα |
|---|---|
| Scanning Speed | 3 deg/min in 2θ |
| Chart Speed | 30 mm/min |
| Count per Minute | 20 K |
| Time Constant | 3 Second |
| Current/Volt | 20 mA / 30 KV |

The X-ray diffraction peaks in 2θ range of 10-85 $^0$ were recorded. The 'd' values and intensity of each peak was tabulated for phase identification from ASTM powder files.

### 3.5.2 Particle Size Determination

The Debye-Sherrer line broadening method was applied for particle size determination. The expression relating particle size, line width 'B' at half intensity for a diffraction line at Bragg's angle $\theta$ has the form

$$t = \frac{0.9\lambda}{B * COS\theta}$$

The breadth of the above equation however refer to, the extra broadening excluding particle size or strain should be zero and if any it is called instrumental broadening, $B_s$. This is evaluated by using similar material of larger grain size (about 2 micron) and measuring the half width of diffraction line in the same angular range as of interest. A correction is applied using following expression to obtain correct line width $B_c$ from the standard

$B_c{}^2 = B^2{}_m - B^2{}_s$

Where,

$B_m$ is the line width of desired peak and

$B_s$ is the instrumental broadening of same angle $\theta$.

In the present case silicon wafer having grain size of about 2 micron was used as a standard. During particle size measurements only those peaks were considered which lie close to the diffraction peaks of desired phases.

## 3.6 Chemical Activity Measurement

The material synthesized in the present investigation has very high internal surface area and expected to be very good absorbent. Thus chemical activity for adsorption was investigated. Out of several methods, the dye adsorption method was adopted. The dye chosen for given work have commercial name, crystal violet dye, the details of this is given below:

Name: Hexamethyleneparaosaniline, Hexamethyl(p-roasahilinium chloride), Methyle Voilet 10B.

Chemical Formula: $C_{25}H_{30}ClN_3$

Solubility: Soluble in water ($25^0$ C) approximately16 g/l.

Ph: 2.5-3.5 (10 g/l, $H_2O$, $20^0$ C)

Melting Point: 189-194 $^0C$.

Bulk Density: 220-400 kg/m$^3$.

Ring Structure:
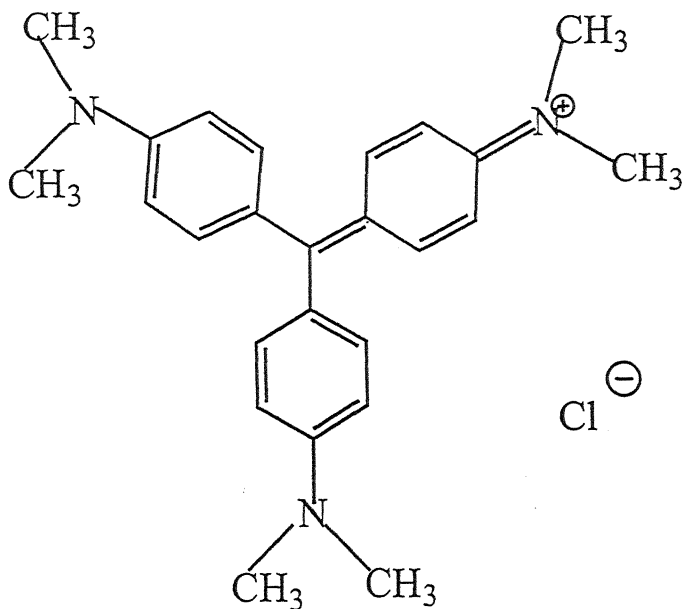


Fig.3.1: Ring Structure of Crystal Violet Dye.

## Dye Absorption Method

The standard solution was prepared by dissolving 0.5mg crystal violet dye in 500 ml distilled water. This standard solution was assumed to contain 100 units of parent color per 100-ml liquor. A series of other solutions were prepared by further dilution of the above solution. Thus 5, 10, 15 to 65 ml of the above solutions was made to 100 cc by adding distilled water. The color of these diluted solutions therefore corresponds to 5, 10, and 15 to 65 % of these solutions. Thus, if 10 ml of standard solution were diluted to 100 ml with distilled water, the color of that mixture would represent a concentration of 10 color units per 100 ml. These solutions were used as reference solutions for comparison of colors.

Two kind of adsorption tests ware carried out

(1) The color adsorption for a fixed time of 20 minutes by different samples.

(2)The progress of adsorption was monitored as a function of time till saturation. These are described in following sections.

## 3.6.1 Fixed Time adsorption

In this case, 0.5 gm of the sample was added to 50 ml of standard solution followed by stirring. This was kept for 20 minutes to allow sufficient time for absorption. The resulting mixture was filtered through whatman paper no. 5 filter paper. The color of the filtrate thus obtained was matched with the reference solutions prepared earlier. The difference in the color units between standard and reference solution gave the percentage of color adsorbed by 0.5 gm of sample having specific material processing history.

## 3.6.2 Time Dependent Adsorption

To carry on time dependent color adsorption study the standard solution is prepared by dissolving 0.3-mg crystal violet dye in 500 ml of solution. The reference solution was prepared as explain earlier. The 0.2-mg sample was added to 25ml of standard solution and color matching was continuously carried out for ½, 1, 2, 3 and 4 minutes till saturation.

# CHAPTER 4

# RESULTS AND DISCUSSIONS

## A. Preparation of Silicon Carbide From Rice Husk

The scanning electron micrographs of rice husk heated at 1280 $^0$C, 1330 $^0$C, 1350 $^0$C and 1380 $^0$C under reducing conditions are shown in Fig.4.1 to Fig. 4.3. Fine needle type SiC whiskers are visible on the husk surface with aspect ratio of around 8.5. Population density of SiC needles seems to be unaffected by the above temperature range. The amount of SiC formed with reference to husk matrix is quite small. As a result no X-ray diffraction peaks are visible for SiC needles in powder X-ray diffractogram.

Figure 4.1: Scanning electron micrograph of Silicon Carbide synthesized at various temperature and at different magnifications.



(a) Temperature =1280 $^0$C, Mag. = 750x

(b) Temperature = 1330 $^0$C, Mag. = 200x
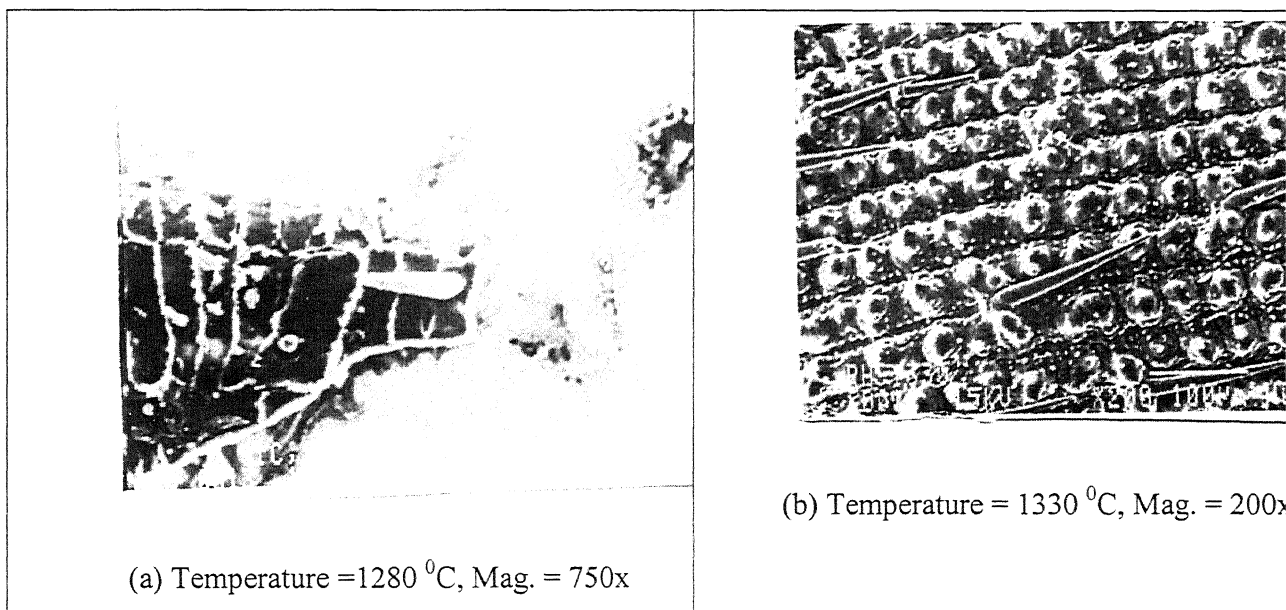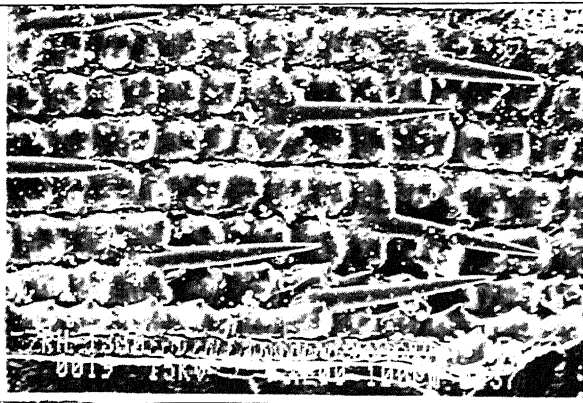
(c) Temperature = 1330 $^0$C, Mag. = 200x
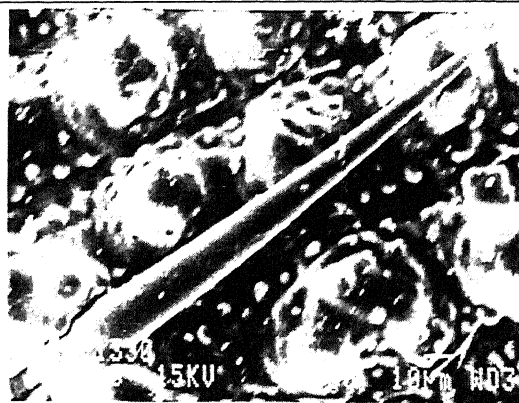
(d) Temperature = 1330 $^0$C, Mag. = 600x
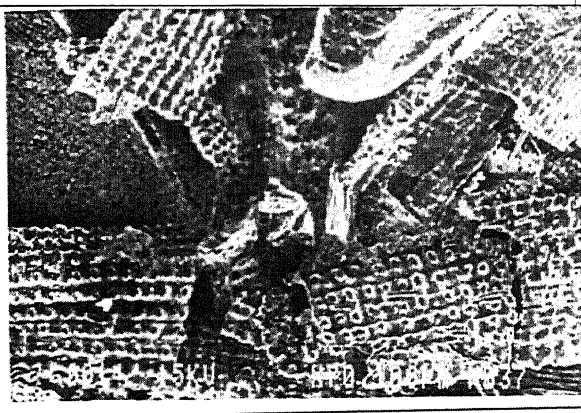
(e) Temperature = 1380 $^0$C, Mag. = 70x
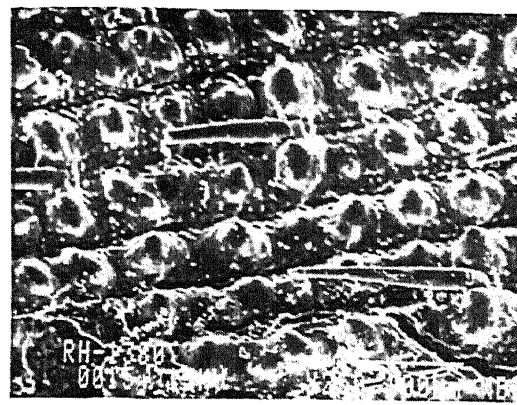
(f) Temperature = 1380 $^0$C, Mag. = 600x

Figure 4.2 : Scanning electron micrograph of Silicon Carbide synthesized at various temperature and at different magnifications.
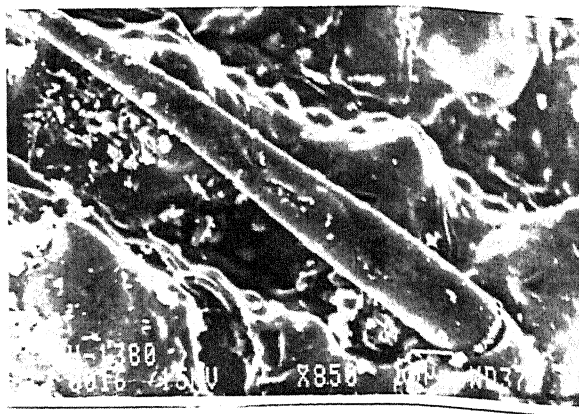
Figure 4.3: Scanning electron micrograph of Silicon Carbide synthesized at temperature of $1380\ ^0\ C$ and Magnification $= 850x$.

# B. Silica Sintered Compact

Rice husk cylindrical silica pallets were produced by compacting the powdered ash. After adding aqueous solution of sodium silicate as a binder, they were subjected to following four major evaluations.

(1) Variation in density of green compacts as a function of compacting pressure, composition(Silica and Sodium Silicate) and sintering temperature.

(2) Variation of mechanical strength of sintering compacts as s function of sintering temperature, binder proportion and compacting pressure.

(3) Effect of sintering temperature on microscopic properties such as specific surface area, porosity and grain size.

(4) Estimation of adsorptive capacity of sintered compact by dye chemisorptions.

The result of present investigation on these lines are therefore presented and discussed below in following section.

Table 4.1: Variation of sintered density with temperature, pressure and binder
Content.

| Sr. No. | Binder | Pressure | Temp ($^0$C) | Green Density (gm/cm$^{3)}$ | Sintered Density (gm/cm$^3$) | Avg. Decreased Density |
|---|---|---|---|---|---|---|
| 1. | Low | 2T | 800 | 0.972 | 0.89 | |
| 2. | Low | 2T | 900 | 1.0687 | 1.018 | 5.03 |
| 3 | Low | 2T | 1000 | 1.0621 | 1.034 | |
| 4 | Low | 2T | 1100 | 1.11 | 1.06 | |
| 5 | Med | 2T | 800 | 1.055 | 0.993 | |
| 6 | Med | 2T | 900 | 0.992 | 0.97 | 2.16 |
| 7 | Med | 2T | 1000 | 0.995 | 0.98 | |
| 8 | Med | 2T | 1100 | 1.025 | 1.015 | |
| 9 | High | 2T | 800 | 0.936 | 0.91 | |
| 10 | High | 2T | 900 | 0.847 | 0.82 | 5.88 |
| 11 | High | 2T | 1000 | 1.017 | 0.992 | |
| 12 | High | 2T | 1100 | 1.08 | 0.93 | |
| 13 | Low | 4T | 800 | 1.5 | 1.132 | |
| 14 | Low | 4T | 900 | 1.19 | 1.149 | 12.92 |
| 15 | Low | 4T | 1000 | 1.375 | 1.115 | |
| 16 | Low | 4T | 1100 | 1.15 | 1.13 | |
| 17 | Med | 4T | 800 | 1.177 | 1.13 | |
| 18 | Med | 4T | 900 | 1.217 | 1.21 | 2.81 |
| 19 | Med | 4T | 1000 | 1.196 | 1.148 | |
| 20 | Med | 4T | 1100 | 1.1 | 1.07 | |
| 21 | High | 4T | 800 | 1.19 | 1.16 | |
| 22 | High | 4T | 900 | 1.166 | 0.857 | 15.82 |
| 23 | High | 4T | 1000 | 1.196 | 0.867 | |
| 24 | High | 4T | 1100 | 1.2 | 1.12 | |
| 25 | Low | 6T | 800 | 1.25 | 1.125 | |

| 26 | Low | 6T | 900 | 1.225 | 1.20 | |
|----|-----|-----|------|-------|-------|------|
| 27 | Low | 6T | 1000 | 1.230 | 1.166 | |
| 28 | Low | 6T | 1100 | 1.27 | 1.15 | |
| 29 | Med | 6T | 800 | 1.3 | 1.26 | |
| 30 | Med | 6T | 900 | 1.326 | 1.236 | 5.36 |
| 31 | Med | 6T | 1000 | 1.374 | 1.341 | |
| 32 | Med | 6T | 1100 | 1.3 | 1.18 | |
| 33 | High | 6T | 800 | 1.254 | 1.239 | |
| 34 | High | 6T | 900 | 1.243 | 1.1219 | 2.27 |
| 35 | High | 6T | 1000 | 1.219 | 1.188 | |
| 36 | High | 6T | 1100 | 1.22 | 1.18 | |

# 4.1 Variation of Bulk Density with Sintering Temperature, Binder Ratio and Compacting Pressure

For compacting pressure of 2 T, the variation of density with sintering temperature of pallets is shown in Fig. 4.4 to Fig. 4.6. It is found that in all these cases green density is always larger than sintered density. Also there seems to be a tendency of increase in density with increasing sintering temperature.

The pallets compacted at 6T are shown in Fig.4.7 to Fig.4.9. Again the green density remains always higher than sintered density. Also sintered density goes through a maxima around $900^0$ C-1000 $^0$C. However in the case of higher binder, density is seems to continuously decreasing with sintering temperature.

The density of compact is directly proportional to compacting pressure as shown in Fig. 4.10. But this is not with the case of binder, the density increases to maximum upto medium binder then it decreases as shown in Fig. 4.11.

Fig. 4.4 Variation of density with sintering temperature for low binder and compaction pressure of 2T.



Fig. 4.5 Variation of density with sintering temperature for medium binder and compaction pressure of 2T.

Fig 4.6: Variation of density with sintering temperature for high binder and compaction pressure of 2T.
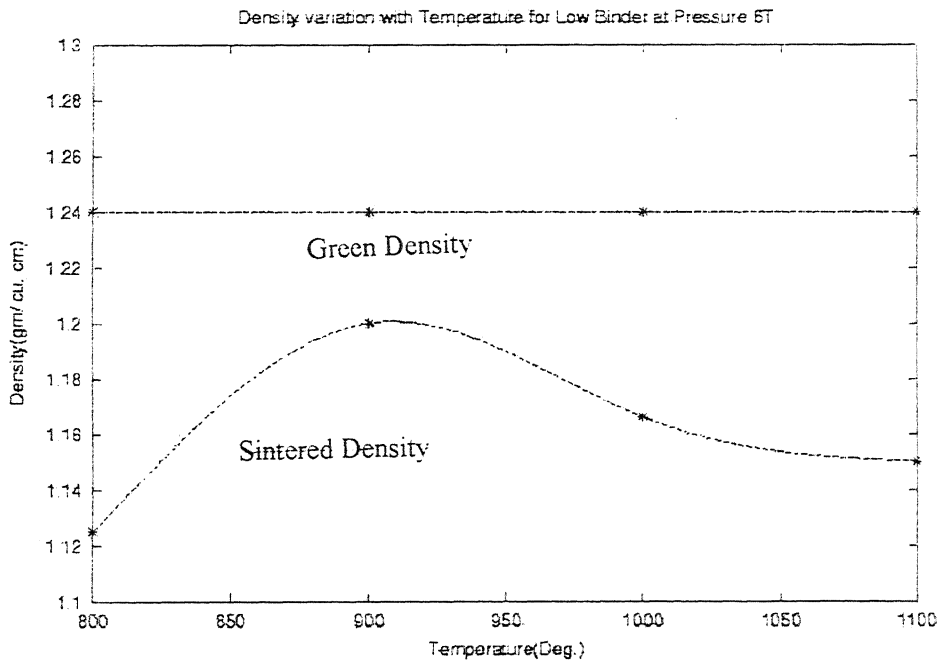


Fig 4.7 : Variation of density with sintering temperature for low binder and compaction pressure of 6T.
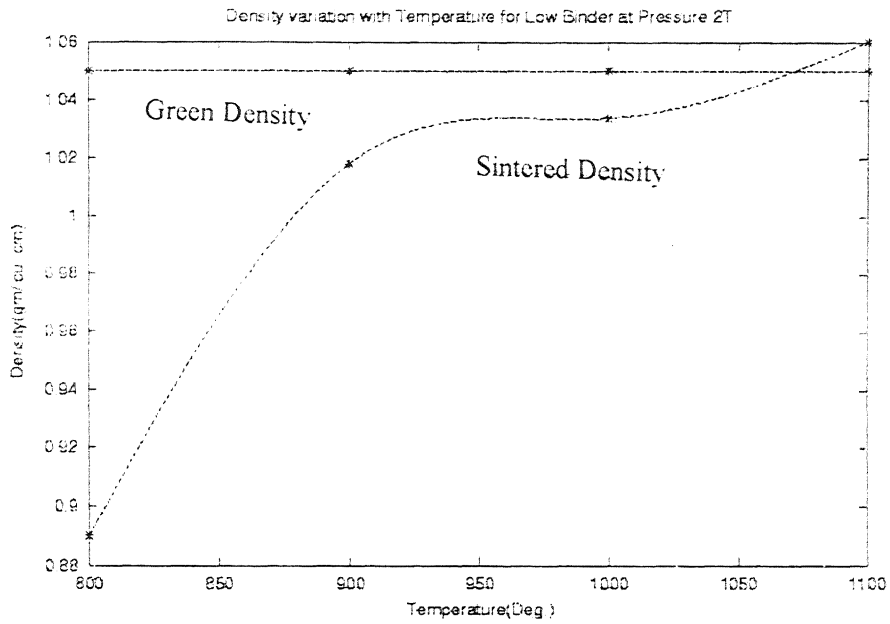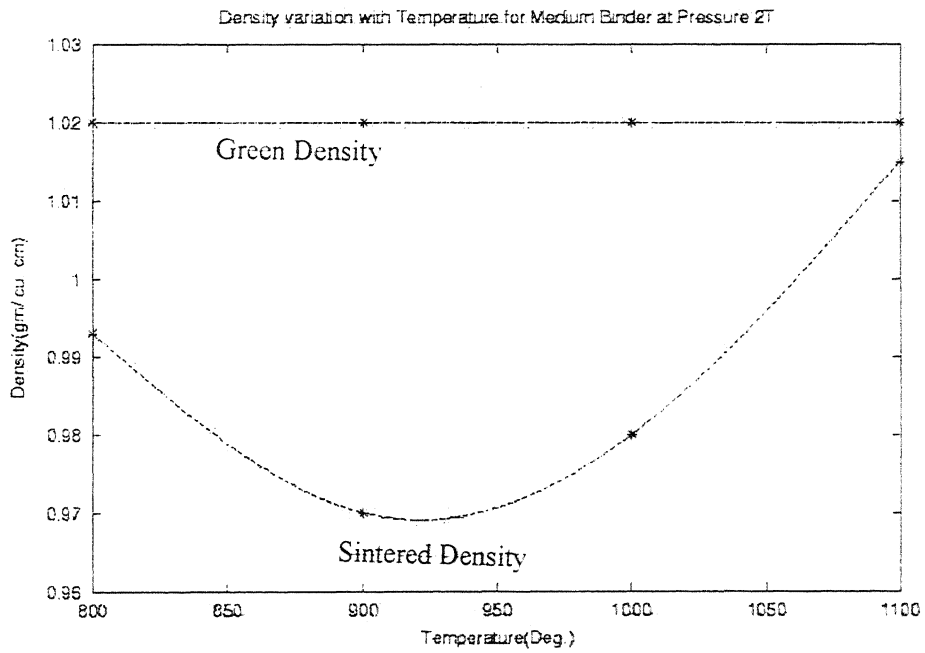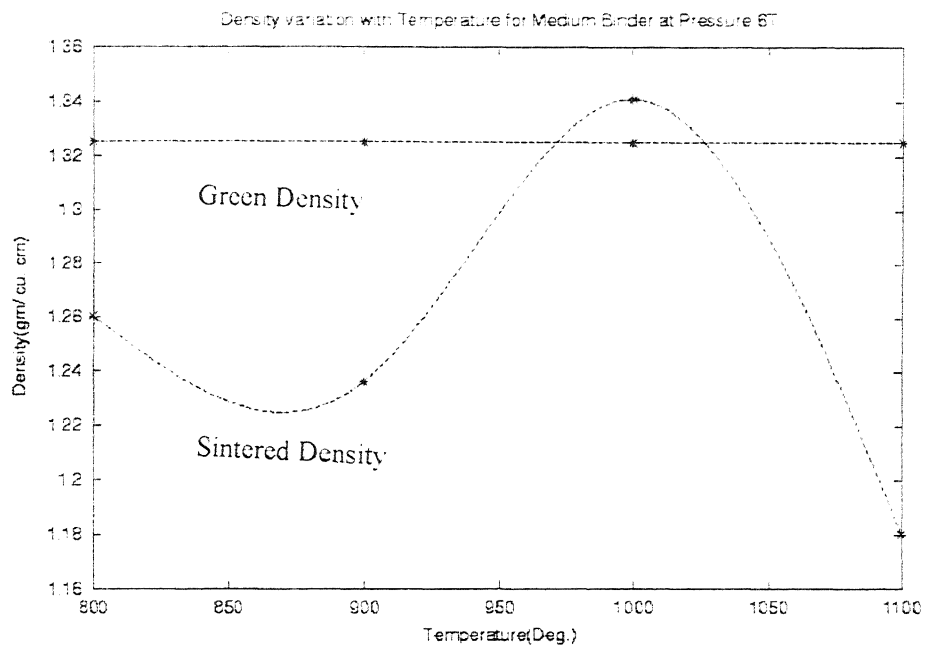
Fig 4.8: Variation of density with sintering temperature for medium binder and compaction pressure of 6T.


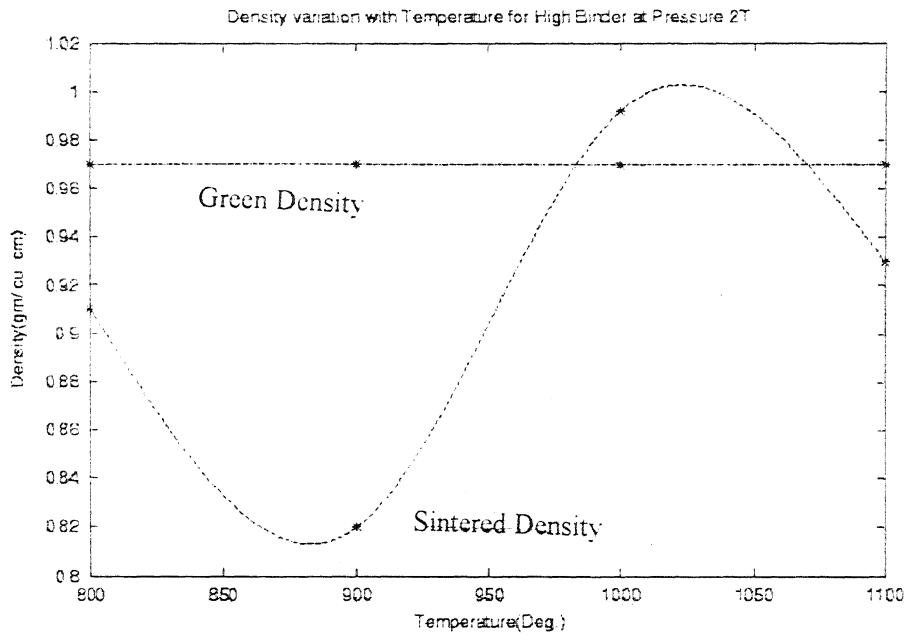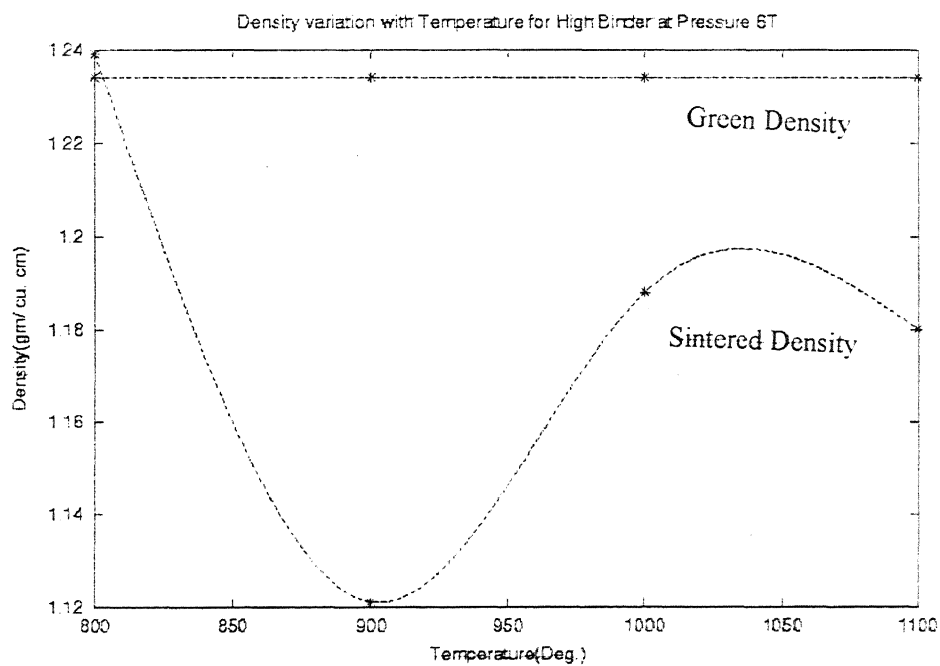
Fig 4..9 : Variation of density with sintering temperature for high binder and compaction pressure of 6T.
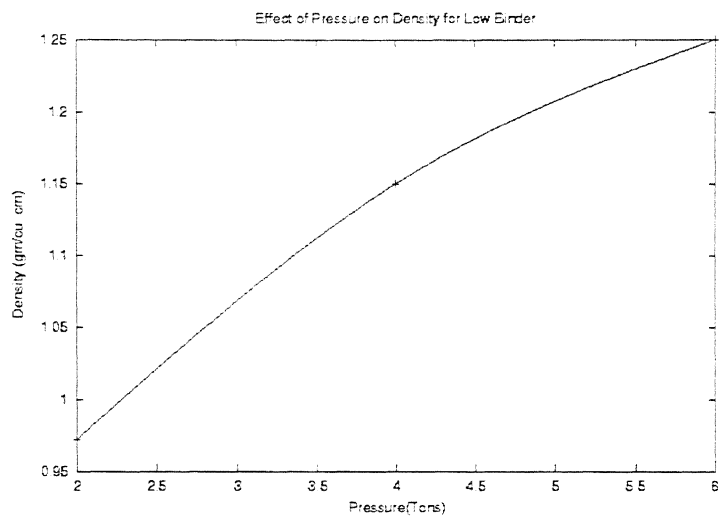
Fig. 4.10: Effect of pressure on density of sintered compacts.
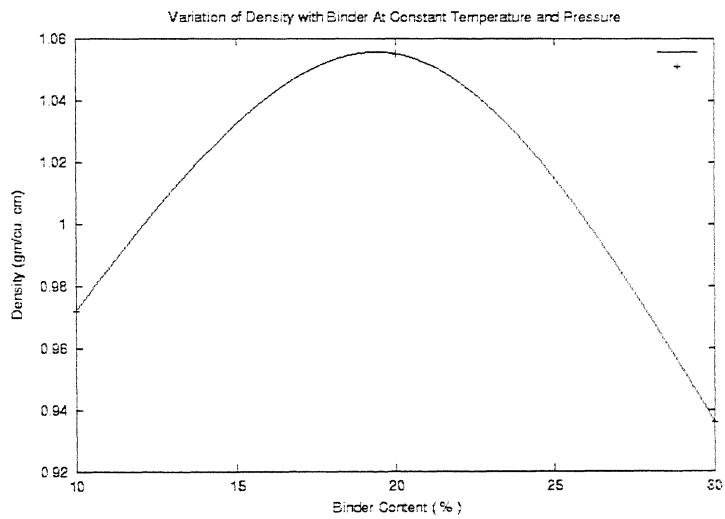


Fig. 4.11: Effect of variation of binder on density of sintered compacts.

Table 4.2: Variation of mechanical strength with temperature, pressure and binder content.

| Sr. No. | Binder | Pressure | Temperature ($^0$C) | Strength (KN/cu. Cm) |
|---------|--------|----------|---------------------|----------------------|
| 1. | Low | 2T | 800 | 0.58 |
| 2. | Low | 2T | 900 | 0.399 |
| 3 | Low | 2T | 1000 | 0.62 |
| 4 | Low | 2T | 1100 | 0.98 |
| 5 | Med | 2T | 800 | 0.23 |
| 6 | Med | 2T | 900 | 0.64 |
| 7 | Med | 2T | 1000 | 0.8 |
| 8 | Med | 2T | 1100 | 1.38 |
| 9 | High | 2T | 800 | 0.29 |
| 10 | High | 2T | 900 | 0.6 |
| 11 | High | 2T | 1000 | 0.8 |
| 12 | High | 2T | 1100 | 0.94 |
| 13 | Low | 4T | 800 | 0.36 |
| 14 | Low | 4T | 900 | 0.85 |
| 15 | Low | 4T | 1000 | 1.14 |
| 16 | Low | 4T | 1100 | 0.9 |
| 17 | Med | 4T | 800 | 0.56 |
| 18 | Med | 4T | 900 | 0.9 |
| 19 | Med | 4T | 1000 | 1.74 |
| 20 | Med | 4T | 1100 | 0.67 |
| 21 | High | 4T | 800 | 0.55 |
| 22 | High | 4T | 900 | 0.62 |
| 23 | High | 4T | 1000 | 1.38 |
| 24 | High | 4T | 1100 | 1.23 |
| 25 | Low | 6T | 800 | 0.42 |

| 26 | Low | 6T | 900 | 0.96 |
| 27 | Low | 6T | 1000 | 1.56 |
| 28 | Low | 6T | 1100 | 0.87 |
| 29 | Med | 6T | 800 | 1.14 |
| 30 | Med | 6T | 900 | 1.29 |
| 31 | Med | 6T | 1000 | 1.38 |
| 32 | Med | 6T | 1100 | 1.35 |
| 33 | High | 6T | 800 | 0.43 |
| 34 | High | 6T | 900 | 0.99 |
| 35 | High | 6T | 1000 | 1.54 |
| 36 | High | 6T | 1100 | 1.3 |

## 4.2 Variation of mechanical strength (fracture strength) of sintered compact with sintering temperature, compacting pressure and proportion of binder

The variation of mechanical strength of sintered compact with binder content of low, medium and high are shown in Fig. 4.12 to Fig. 4.14.

In case of pallet pressurized at 2T, following two important conclusions can be drown:

(1)     The strength of pallets increases with temperature from $800^0$ C to $1100^0$ C.

(2)     The medium binder shows the maximum mechanical strength compare to low and high binder.

In case of pallets pressurized at 4T, the following conclusions can be made:

(1)     The strength of the pallets is found to be increased with increase in temperature up to $1000^0$ C. Beyond $1000^0$ C, the mechanical strength shows decreasing trend.

(2)     Again the sample with medium binder showed the maximum strength
Compare to other binder at $1000^0$ C.

The pallets pressed at 6T also shows similar trends exhibits similar trend as those exhibited by compacting pressure of 4 Tons. The sample with low and medium binder shows maximum strength.
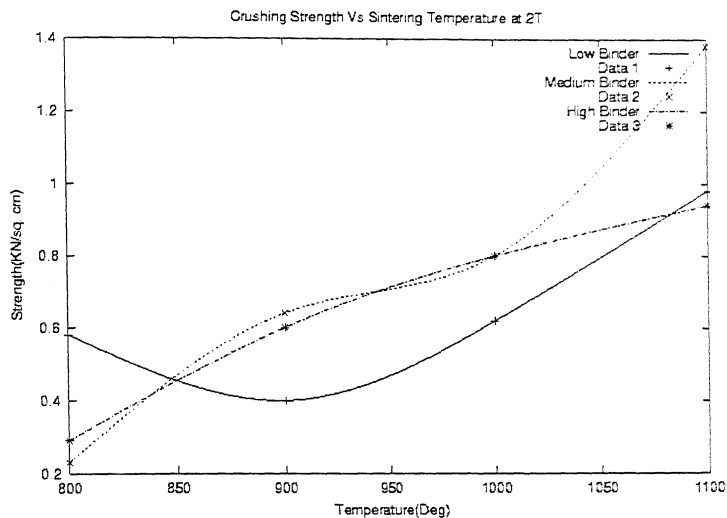


Fig. 4.12: Variation of crushing strength of compacts with sintering temperature at compaction pressure of 2T for different binder composition.
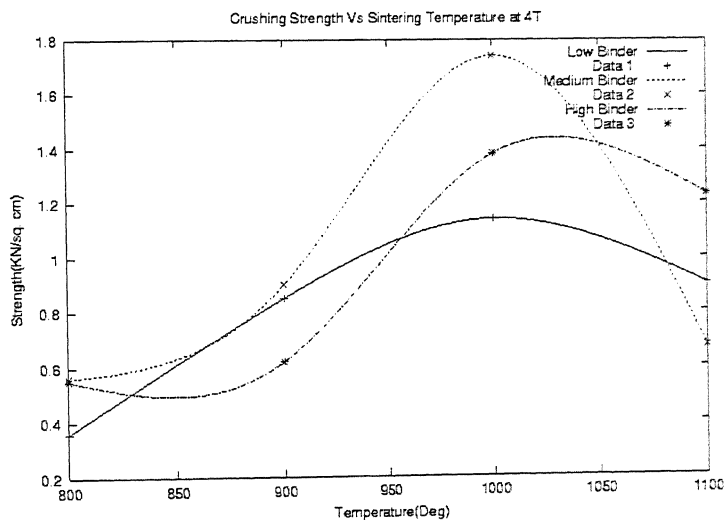


Fig. 4.13: Variation of crushing strength of compacts with sintering temperature at compaction pressure of 4T for different binder composition
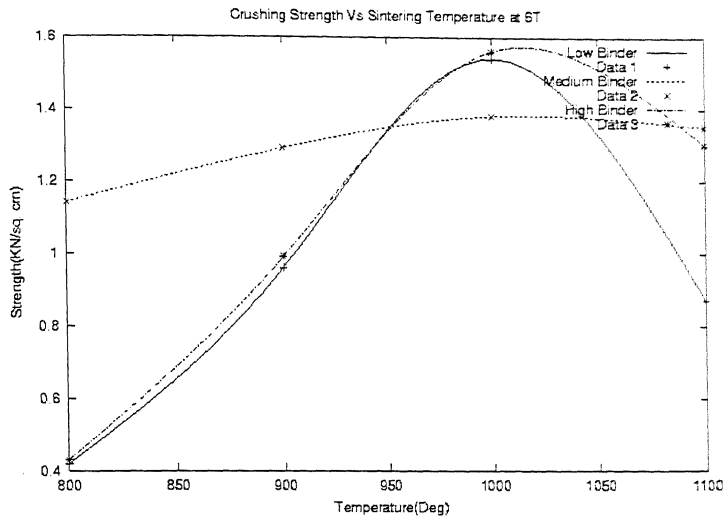
Fig. 4.14: Variation of crushing strength of compacts with sintering temperature at compaction pressure of 6T at different binder composition

# 4.3 Variation of Mechanical Strength with Compacting Pressure

The variation of mechanical strength with compacting pressure is shown in Fig. 4.15 to Fig. 4.17. In all the cases, mechanical strength is found to be increased with compacting pressure.
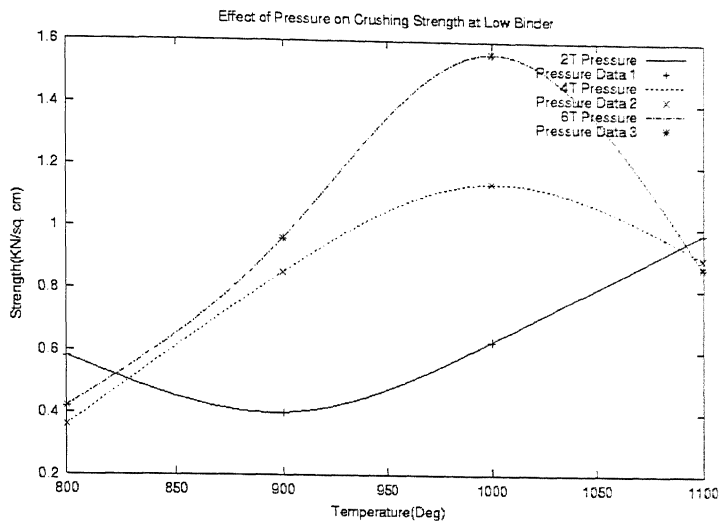
Fig. 4.15: Variation of crushing strength of sintered compacts with compacting pressure at low binder.
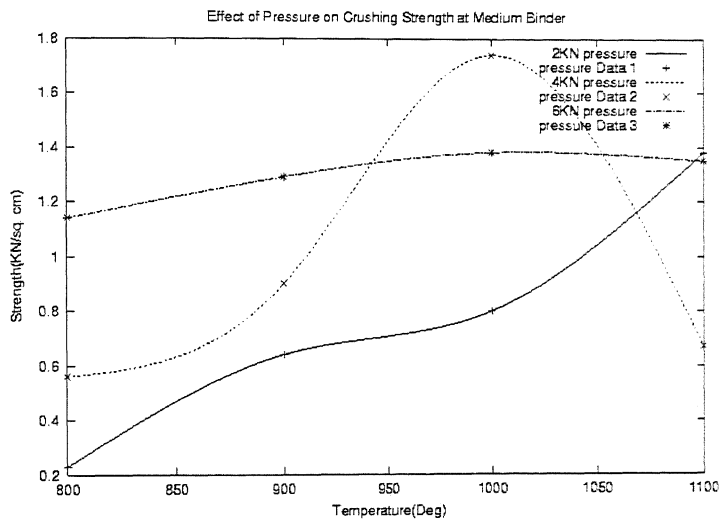


Fig. 4.16: Variation of crushing strength of sintered compacts with compacting pressure at medium binder.

Effect of Pressure on Crushing Strength at High Binder
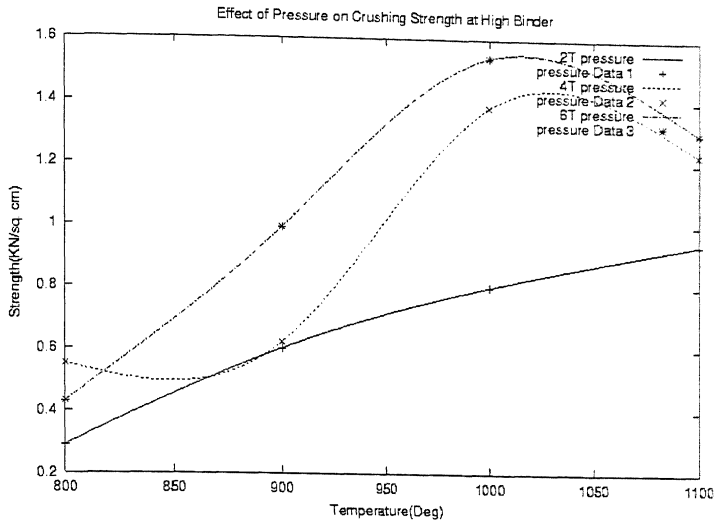
Fig. 4.17: Variation of crushing strength of sintered compacts with compacting pressure at high binder.

## 4.4 X-Ray Diffraction

### 4.4.1 X –Ray Diffraction pattern

The X-Ray diffraction pattern of white rice husk ash shows an amorphous structure without any distinguishable peaks indicating presence of Silica in amorphous state. X – Ray diffraction pattern of all the samples prepared above temperature 800 ° C with low to high binder exhibited sharp peaks at $2\theta = 22°$, $31.5°$ and $36°$ which matched with low or $\alpha$-crystobalite structure.

Table 4.3 : Variation of particle size with Sintering temperature.

| Sr. No | Binder | Temperature ($^0$C) | d-values | Paricle Size(A$^0$) | | | Average |
|---|---|---|---|---|---|---|---|
| 1. | Low | 800 | 4.04,2.84,2.48 | 149.1 | 193.5 | 242.5 | 195.06 |
| 2. | Med | 800 | 4.04,2.85,2.43 | 160.81 | 163.81 | 183.71 | 173.76 |
| 3. | High | 800 | 4.04,2.84,2.49 | 211.90 | 215.98 | 180.87 | 198.42 |
| 4. | Low | 900 | 4.04,2.82,2.46 | 143.67 | 182.67 | 195.8 | 174.05 |
| 5. | Med | 900 | 4.26,4.04,2.47 | 153.45 | 159.22 | 151.23 | 154.63 |
| 6. | High | 900 | 4.04,2.82,2.48 | 170.67 | 146.92 | 160.67 | 159.42 |
| 7. | Low | 1000 | 4.04,3.79,2.47 | 131 | 176.85 | 168.04 | 158.63 |
| 8. | Med | 1000 | 4.04,2.84,2.47 | 139.27 | 157.68 | 141.65 | 146.2 |
| 9. | High | 1000 | 4.04,2.84,2.48 | 138.19 | 147.61 | 169.15 | 151.65 |
| 10. | Low | 1100 | 4.04,2.84,2.48 | 121.91 | 106.12 | 140.06 | 122.7 |
| 11. | Med | 1100 | 4.04,2.84,2.48 | 119.51 | 149.59 | 130.28 | 133.13 |
| 12. | High | 1100 | 4.08,2.87,2.48 | 131.17 | 136.49 | 131.94 | 133.18 |

## 4.4.2 Variation of particle size with temperature

As explained in section [2.5.1], the X – Ray diffraction can also be used for determination of particle size. As shown in Fig. 4.18, the particle size decreases with temperature. The pallets having medium binder shows minimum particle size at sintering temperature of 1000 $^0$C,

Table 4.4:Variation of surface area with sintering temperature .

| Sr. No. | Sample | Binder | Temperature ($^0$C) | Surface Area (sq. m/g) | Pore Volume (ml/g) |
|---------|--------|--------|---------------------|------------------------|---------------------|
| 1. | White Ash (Virgine) | ------- | 600 | 176.78 | 0.1360 |
| 2. | White Ash (Pellet Granules) | Med | 800 | 34.829 | 0.0082 |
| 3. | White Ash (Pellet Granules) | Med | 900 | 1.207 | 0.0050 |
| 4. | White Ash (Pellet Granules) | Med | 1000 | 0.284 | ------- |
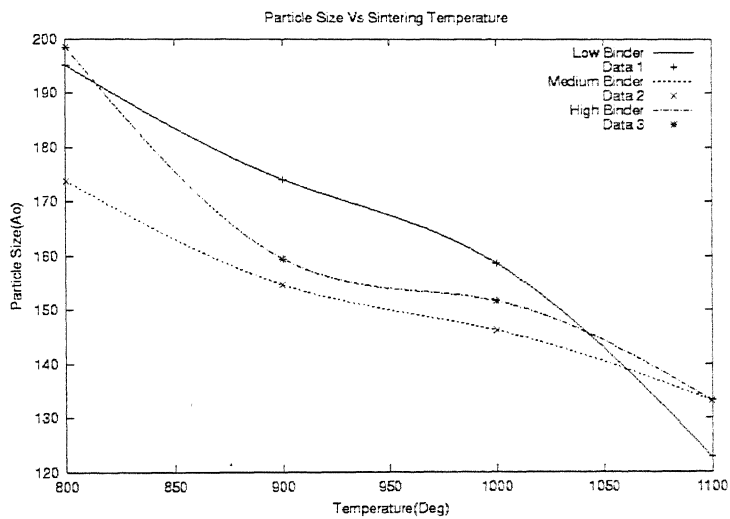


Fig. 4.18: Variation of particle size of the compact with sintering temperature.

## 4.5 Variation of Surface Area with temperature

As shown in table 4.4 and Fig. 4.19, the BET surface area and pore volume of sample decreases with sintering temperature. The initial white rice husk ash which is obtained after burning rice husk at 600° C, shows very high surface area. After sintering to 800° C with sodium silicate binder it drops down to 34.829 sq. m/g. After 800° C the surface area touches to 1.207 sq. m/g and decreases further. The pore volume also shows decreasing trend with temperature.
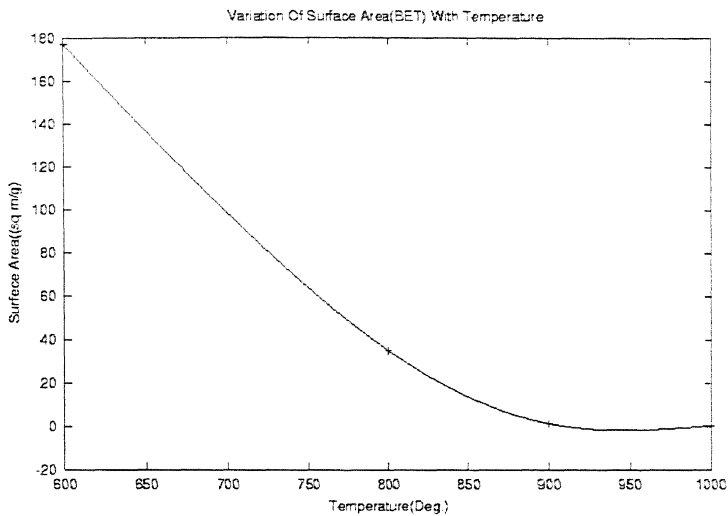
Fig. 4.19: Variation of surface area of compact with sintering temperature.

## 4.6 Chemical Activity Test

The chemical activity of the white ash sample is measured by color absorption of water-soluble crystal violet dye.

# 4.6.1 Color Absorption As a Function of Sintering Temperature of Samples

The amount of color absorbed for a fixed time (20 minutes) by samples (low, medium and high binder) sintered at $800^0$ C to $1100^0$ C is presented in table [6].

The plot between amount of absorption and sintering temperature is shown in Fig.4.20.As shown in Fig. 4.20, the percent decolorization decreases with temperature. The reason may be due to decrease in surface area with sintering temperature as shown earlier. As the surface area decreases, the less will be site available for color absorption.. Therefore it shows decreasing trend of color absorption with temperature. At high temperature i.e. above $1000^0$ C, there is no effect on absorption and it remains constant. Also binder content has effect on absorption. As shown in table 4.5, the percent color decolorization decreases with increase in binder content from low to medium after that it remains constant.

Table 4.5: Percent decolorization of crystal violet dye at constant time.

| Sr. No | Binder | Temperature ($^0$C) | Time (Minutes) | Percent Decolorization |
|--------|--------|--------------------|--------------|----------------------|
| 1. | Low | 800 | 20 | 65 |
| 2. | Low | 900 | 20 | 60 |
| 3. | Low | 1000 | 20 | 55 |
| 4. | Low | 1100 | 20 | 55 |
| 5. | Med | 800 | 20 | 60 |
| 6. | Med | 900 | 20 | 55 |
| 7. | Med | 1000 | 20 | 50 |
| 8. | Med | 1100 | 20 | 50 |
| 9. | High | 800 | 20 | 60 |
| 10. | High | 900 | 20 | 55 |
| 11. | High | 1000 | 20 | 50 |
| 12. | High | 1100 | 20 | 50 |
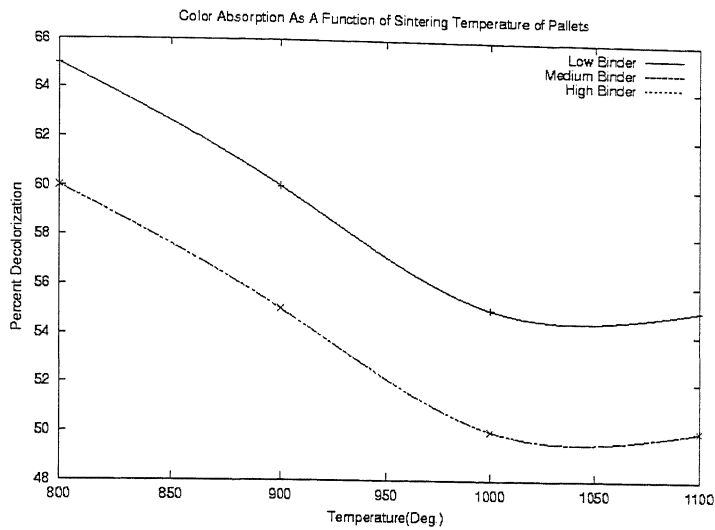
Fig. 4.20: Color absorption as a function of sintering temperature of the compact.

## 4.6.2 Color Absorption With Time

The result of color adsorption is presented in table 4.6. As shown in Fig. 4.21 to Fig. 4.23, the color adsorption increases with time and seem to saturate quickly after a period of about 120 seconds. The amount 'Y' of the color absorption as a function of time 't' can be expressed as

$$Y = A\,t^m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(I)$$

where coefficient 'A ' and exponent 'm' are constants of material. Thus plotting the value of log Y with log t gives the value of 'A' and 'm' respectively as presented in table 4.6. Thus the expression (I) under this condition can be written as :

$$Y = (\pm 6.045) * t^{(\pm 0.0025)}$$

The increase in amount of binder seems to lower the amount of decolorization with time.

Table 4.6: Color adsorption with time for samples with different    binder content and sintering temperature.

| Sr No | Temp ($^0$C) | Binder | Percent Decolorizatin Time (seconds) | | | | | Coefficient (A) | Exponent (m) | Deviation |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 0 | 60 | 120 | 180 | 240 | | | |
| 1. | 900 | Low | 0 | 50 | 55 | 55 | 55 | 35.85 | 0.09 | -0.008 |
| 2. | 1000 | Low | 0 | 45 | 50 | 50 | 50 | 38.62 | 0.07 | -0.03 |
| 3. | 1100 | Low | 0 | 45 | 50 | 50 | 50 | 38.62 | 0.07 | -0.03 |
| 4. | 900 | Med | 0 | 45 | 50 | 50 | 50 | 32.53 | 0.09 | -0.01 |
| 5. | 1000 | Med | 0 | 40 | 45 | 45 | 45 | 26.84 | 0.1 | 0.01 |
| 6. | 1100 | Med | 0 | 40 | 45 | 45 | 45 | 26.84 | 0.1 | 0.01 |
| 7. | 800 | High | 0 | 45 | 50 | 50 | 50 | 32.53 | 0.09 | -0.02 |
| 8. | 900 | High | 0 | 40 | 45 | 45 | 45 | 26.53 | 0.1 | 0.01 |
| 9. | 1000 | High | 0 | 35 | 40 | 40 | 40 | 29.66 | 0.08 | -0.01 |
| 10. | 1100 | High | 0 | 35 | 40 | 40 | 40 | 29.66 | 0.08 | -0.01 |

Average Exponent   = 0.0966
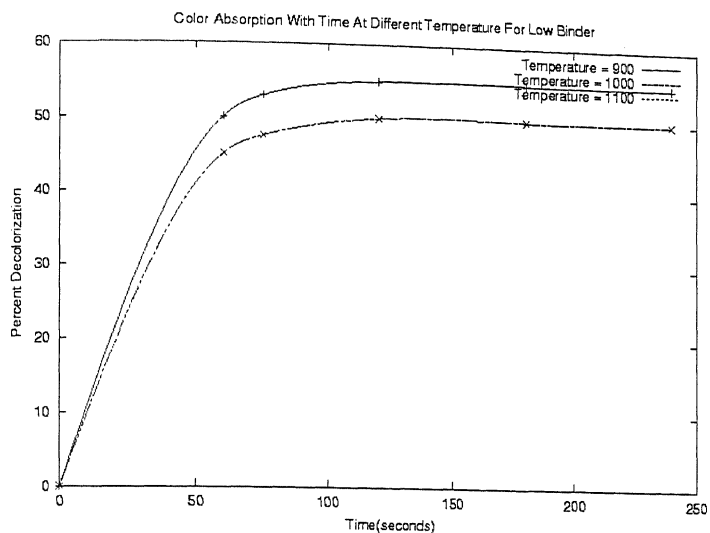
Average Coefficient = 31.37

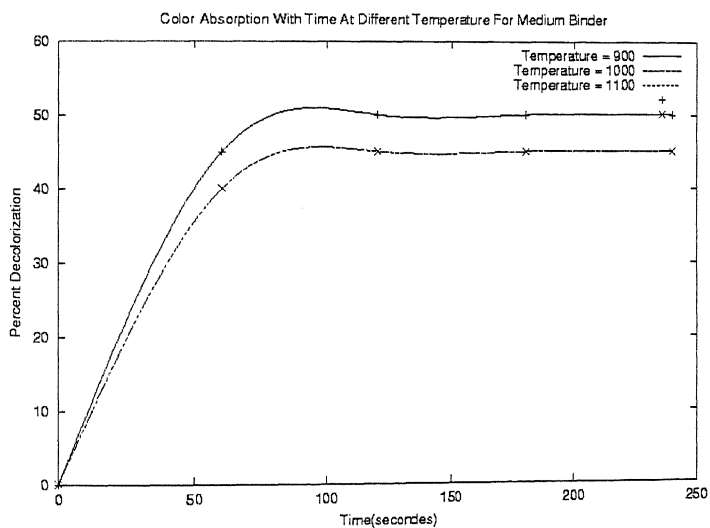Fig.4.21: Variation of color adsorption with time for low binder compact.



Fig. 4.22 : Variation of color adsorption with time for medium binder compact.
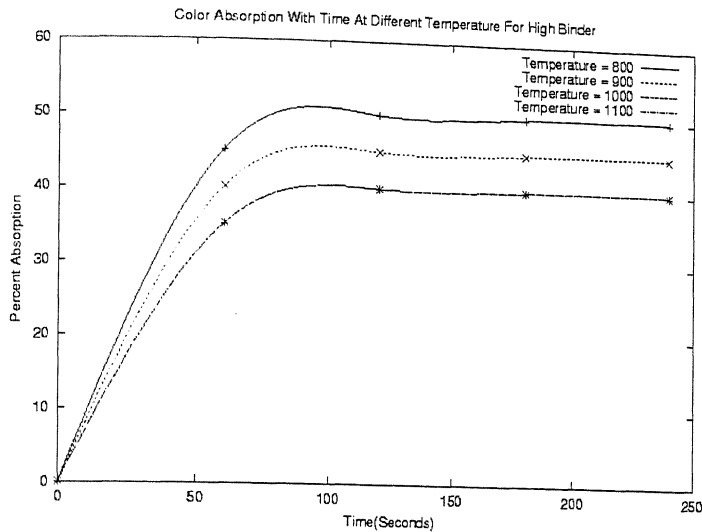
Fig. 4.23: Variation of color adsorption with time for high binder compact.

## 4.7 Discussion

The rice husk prepared at temperature around 800 $^0$C in open atmosphere is amorphous and it transformed to α-cristobalite above 800 $^0$C as observed by X-ray diffraction. This structural transformation is also accompanied by massive decrease in internal surface area and porosity of the rice husk as observed by BET measurement. Similar observation has been made by Didamony et al.[16] and Rao et al.[12]. Observation of decreasing amount of dye adsorption with increasing sintering pallet temperature is thus a direct consequence of decreasing internal surface area with processing temperature. Similar observations has been made by Basu et al.[12].

Behavior of increasing densification with increasing sintering temperature for 2 Ton compacting pressure is as expected. However decrease in densification after 900 $^0$C-1000 $^0$C for pallets compacted at 6 Ton is quite curious to interpret. The effect of compacting pressure on densification shows a linear relation between densification and compacting pressure. This can be understood in terms of increasing chance of coalescence amongst powder particles with increasing amount of compaction ( i. e.

compacting pressure). The same is not true with binder proportion. Densification goes through maxima at medium proportion of binder as shown in Fig. 4.11.

The mechanical strength for all binder at compaction pressure of 2Ton shows a increasing trend with increasing sintering temperature as expected. This result is quite similar to one with increasing densification with increasing sintering temperature as discussed earlier. However pallets compacted at 4 and 6 Ton show different mechanical behaviors. The mechanical strength passes through maxima at around 1000 $^{0}$C of sintering temperature. It is interesting to note that densification behavior for compacting pressure of pallets compacted at 6 Ton was quite identical and clearly indicate a direct relation between densification and mechanical strength of the porous material.

# CHAPTER 5

# CONCLUSIONS

The rice husk ash prepared at 800°C in an open atmosphere shows amorphous structure. vever heating above 800°C it gets transformed into $\alpha$ - crystobalite form.

The specific surface area, porosity and adsorption capacities were found to decrease with ering temperature of rice husk pallets containing sodium silicate as binder.

Density of pallets was found to increase with sintering temperature for compacting pressure T. However pallets compacted at 6 T show decrease in density after 900°-1000°. The ts with medium binder(16%) show the maximum density at 1000°C

The mechanical strength of pallets compacted at 2 T increases with sintering temperature. vever the pallets compacted at 4 and 6 T shows the maximum strength at 1000°C of ering temperature and then it decreases. Again the pallets with medium binder showed imum mechanical strength.

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